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CLAIMS

[Claim(s)]

[Claim 1] $(1-x-y)$ Oxygen ion ***** characterized by the bird clapper from the constituent which becomes $ZrO_{2-x}Sc_2O_{3-y}Al_2O_3$.

[Claim 2] $(1-x-y)$ $ZrO_{2-x}Sc_2O_{3-y}Al_2O_3$ ($0.07 \leq x+y \leq 0.13$ and $0.005 \leq y \leq 0.02$) -- oxygen ion ***** according to claim 1 characterized by the bird clapper from a constituent

[Claim 3] $(1-x-y)$ The solid fuel cell characterized by using oxygen ion ***** which has the composition which becomes $ZrO_{2-x}Sc_2O_{3-y}Al_2O_3$ as a solid electrolyte.

[Claim 4] $(1-x-y)$ $ZrO_{2-x}Sc_2O_{3-y}Al_2O_3$ ($0.07 \leq x+y \leq 0.13$ and $0.005 \leq y \leq 0.02$) -- the solid fuel cell according to claim 3 characterized by using oxygen ion ***** which has composition as a solid electrolyte

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to oxygen ion ***** and a solid fuel cell.

[0002]

[Description of the Prior Art] In recent years, an interest is increasing in the solid electrolyte fuel cell using oxygen ion *. From a viewpoint especially of a deployment of energy, the solid fuel cell has the feature which does not receive restrictions of the Carnot efficiency and which was [expect / still better environmental preservation / essentially have a high energy conversion efficiency and] excellent.

[0003] 1000-degree C elevated-temperature operation is required to obtain sufficient ionic conductivity in the 2OY3 stabilization ZrO₂ (YSZ) which is oxygen ion * by which promising ** has been conventionally carried out most as an electrolyte of a solid electrolyte fuel cell.

[0004] However, at such an elevated temperature, degradation of the part life by the reaction with an electrode interface is intense, therefore the present condition is that utilization of a solid fuel cell is behind. To lower operating temperature from such a viewpoint is desired, therefore an appearance of the ion **** material of ionic conductivity higher than YSZ is desired.

[0005] Generally, by oxygen ion ***** of a zirconia system, there is an inclination for ionic conductivity to go up, so that the ionic radius of a dopant becomes small. This is because the activation energy of the oxygen ion which can move becomes small, when the ionic radius of a dopant approaches the ionic radius of Zr⁴⁺. In fact, it is known that 2OZrO₂-Sc₂O₃ system has the highest ionic conductivity by the zirconia system.

[0006] However, with the increase in a dopant, in the field in which the crystal structure changes to a monoclinic system-rhombohedral-cubic, and ionic conductivity takes the greatest value, a rhombohedron becomes stable at a room temperature and a cubic is not stabilized. Above 650 more degrees C, it becomes practically impossible to cause destruction by the heat cycle, in order to carry out tectofacies transition at a cubic, and to use it as a solid electrolyte material.

[0007]

[Problem(s) to be Solved by the Invention] this invention -- YSZ -- a ratio -- BE ** ionic conductivity is high, there is no structure transformation between a room temperature and operating temperature, and it aims at offering practically still more nearly usable oxygen ion ***** also as a solid electrolyte of a fuel cell, and a solid fuel cell

[0008]

[Means for Solving the Problem] Oxygen ion ***** of this invention is ZrO(1-x-y)₂-xSc₂O₃-yAl₂O₃. It is characterized by the bird clapper from composition.

[0009] Moreover, the solid fuel cell of this invention is characterized by using oxygen ion ***** which consists of composition which becomes ZrO(1-x-y)₂-xSc₂O₃-yAl₂O₃ as a solid electrolyte.

[0010] In addition, the above oxygen ion ***** are obtained by the sintering process by the usual

solid phase reaction.

[0011]

[Function] It explains with the knowledge which obtained [acting this invention and] this invention on the occasion of the following.

[0012] this invention person solved the cause of in why ablation between electrodes arises, when it used for a fuel cell first by making ion ***** of $2\text{OZrO}_2\text{-Sc}_3$ system into a solid electrolyte.

Consequently, ablation acquired knowledge that it will be generated for the following reasons.

[0013] That is, with the increase in a dopant, in the field in which the crystal structure changes with a monoclinic system-rhombohedral-cubic, and ionic conductivity takes the greatest value, a rhombohedron becomes stable at a room temperature and a cubic is not stabilized. Above 650 more degrees C, in order to change structurally to a cubic, based on a difference of coefficient of thermal expansion, it is thought that it is what causes the destruction (ablation) by the heat cycle.

[0014] Then, many experiments were repeated and this invention person did the originality pursuit to search for the means for preventing this phase transformation. However, I hear that it must make ionic conductivity higher than YSZ hold, and there is while it is inadequate just to prevent phase transformation as for the point of having required cautions and it can prevent phase transformation.

[0015] Moreover, in process in which many experiments are repeated, it found out that the phase structure stabilized when the subdopant other than Sc was added is acquired, and this invention person may show high ionic conductivity.

[0016] Then, when the experiment was repeated further and a part of Sc was replaced with aluminum with trivalent [stable], the knowledge of cubic structure being stabilized and being acquired was carried out.

[0017] Furthermore, the sum total content of Sc and a subdopant which is the main dopant was making one factor, and the desirable thing was solved, when obtaining still higher conductivity, if it is an addition within a certain limited limits.

[0018] In this invention, the material which consists of composition which becomes $\text{ZrO}(1-x-y)_2\text{-xSc}_2\text{O}_3\text{-yAl}_2\text{O}_3$ is used.

[0019] That is, oxygen ion ***** obtained by this invention contains Sc as a main dopant. Since the ionic radius of Sc is close to Zr, it is easy to move oxygen ion from YSZ. for this reason, YSZ -- a ratio -- remarkable big ionic conductivity is realizable by BE *****

[0020] Moreover, in this invention, aluminum with trivalent [stable] is added as a subdopant. this subdopant -- ionic conductivity -- almost -- the property of Sc -- holding -- in addition -- and the crystal structure is stabilized by the cubic and the crystal transformation in an elevated temperature does not appear In this case, aluminum 2O_3 is not as general sintering assistant **, and is working as suppression of a crystal transformation.

[0021] Furthermore, it is referred to as $0.07 \leq x+y \leq 0.13$ and $0.005 \leq y \leq 0.02$ in this invention. There are no addition, then phase transformation in this limited range, and oxygen ion ***** which has still higher ionic conductivity is obtained.

[0022] Moreover, although ionic conductivity decreased slightly when this invention person faced producing the sintered compact of $2\text{OZrO}_2\text{-Sc}_2\text{O}_3\text{-aluminum}_3$ system of this invention and little addition of SiO_2 was carried out as sintering assistant **, not changing also solved the relative effect.

[0023] By considering as the above composition, a strong (for example, ablation with an electrode does not arise) material of high ionic conductivity and the mechanical strength to a heat cycle is realizable.

[0024]

[Example] The example of this invention is explained below. In addition, although it is natural, this invention is not limited to the following examples.

[0025] (Example 1)

(1-x-y) After blending $\text{ZrO}_2\text{-xSc}_2\text{O}_3\text{-yAl}_2\text{O}_3$ ($0 < x+y < 0.16$ and $x > 0, y > 0$) by the chemical

composition shown in Table 1, it mixed enough, baking was performed for what was cast to ** let with a 20mmphi thickness of 2mm at the temperature of 1620 degrees C for 60 hours in air, and ion ***** was produced. After identifying the generation phase of a sample by the powder X diffraction and carrying out the sweep of the ionic conductivity on the frequency of 10Hz - 1MHz by the impedance meter, it measured by performing an impedance plot.

[0026] The X-ray diffraction pattern in the room temperature in the case of 0.88ZrO(s)2-0.115Sc2O3-0.005aluminum 2O3 is shown in drawing 1 (drawing 1 (a)). In addition, also in 0.88ZrO(s)2-0.12Sc 2O3 which does not contain a subdopant, it is shown (drawing 1 (b)). When a dopant is not included, at a room temperature, a rhombohedron phase is obtained as a single phase. However, if temperature is raised, it will transfer to a cubic near 650 degree C. However, it turns out that the cubic is stabilized by addition of a subdopant.

[0027] The temperature dependence of ionic conductivity is shown in drawing 2 . At 0.88ZrO(s)2-0.12Sc 2O3 which has not added aluminum 2O3, it is the crystal structure. In connection with phase transition, ionic conductivity changes nonsequentially near transition temperature (drawing 2 (b)). Ionic conductivity is mostly satisfied [with 0.88ZrO2-0.115Sc2O3-0.005Al 2O3 which added aluminum 2O3] of the relation of almost linear ARERIUUSU (drawing 2 (a)). Even when aluminum 2O3 is doped, the outstanding ion conductivity is indicated to be $8.9 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 800 degrees C.

[0028] The result of 800 degrees C [which was measured like the following] ionic conductivity is shown in Table 1. The ionic conductivity higher than value 2×10^{-2} of YSZ in 800 degrees C in any case was shown, and, as for the crystal structure, the cubic was stabilized to the room temperature.

[0029] In addition, although ionic conductivity decreases slightly when little addition of SiO2 is carried out as sintering assistant **, the relative effect does not change.

Table 1 Material Conductivity (ohm-1cm-1)

0. 88ZrO2-0.115Sc2O3-0.005Aluminum 2O3 8.8×10^{-2} 0.88ZrO2-0.10Sc2O3-0.02aluminum 2O3 7.1×10^{-2} 0.88ZrO2-0.08Sc2O3-0.04aluminum 2O3 6.2×10^{-2} 0.88ZrO2-0.06Sc2O3-0.06aluminum 2O3 5.1×10^{-2} 0.88ZrO2-0.04Sc2O3-0.08aluminum 2O3 4.8×10^{-2} 0.88ZrO2-0.02Sc2O3-0.10aluminum2O3 2.2×10^{-2}

[0030] (Example 2)

(1-x-y) After blending ZrO2-xSc2O3-yAl 2O3 ($0.07 \leq x+y \leq 0.13$ and $0.005 \leq y \leq 0.02$) by the chemical composition shown in Table 2, it mixed enough, baking was performed for what was cast to ** let with a 20mmphi thickness of 2mm at the temperature of 1620 degrees C for 60 hours in air, and ion ***** was produced. After identifying the generation phase of a sample by the powder X diffraction and carrying out the sweep of the ionic conductivity on the frequency of 10Hz - 1MHz by the impedance meter, it measured by performing an impedance plot.

[0031] As for the crystal structure, a rhombohedron phase did not appear by the subdopant aluminum 2O3, but the cubic was stabilized to the room temperature. The result of 800 degrees C [which was measured like the example 1] ionic conductivity is shown in Table 2.

[0032] In $0.005 \leq y \leq 0.02$, in any case, the high ionic conductivity of 3 times was shown from value 2×10^{-2} of YSZ in 800 degrees C, and, as for the crystal structure, the cubic was stabilized to the room temperature.

[0033] In addition, although ionic conductivity decreases slightly when little addition of SiO2 is carried out as sintering assistant **, the relative effect does not change.

table 2 Material Conductivity (ohm-1cm-1) 0.88ZrO2-0.115Sc2O3-0.005aluminum 2O3 8.9×10^{-2} 0.88ZrO2-0.110Sc2O3-0.010aluminum 2O3 8.6×10^{-2} 0.88ZrO2-0.105Sc2O3-0.015aluminum 2O3 8.3×10^{-2} 0.88ZrO2-0.100Sc2O3-0.020aluminum2O3 8.1×10^{-2} 0.88ZrO2-0.095Sc2O3-0.025aluminum 2O3 5.7×10^{-2}

[0034] (Example 3)

(1-x-y) After blending ZrO2-xSc2O3-yAl 2O3 ($0 < x+y < 0.16$ and $x > 0, y > 0$) by the chemical

composition shown in Table 3, it mixed enough, baking was performed for what was cast to ** let with a 20mmphi thickness of 2mm at the temperature of 1620 degrees C for 60 hours in air, and ion ***** was produced. After identifying the generation phase of a sample by the powder X diffraction and carrying out the sweep of the ionic conductivity on the frequency of 10Hz - 1MHz by the impedance meter, it measured by performing an impedance plot.

[0035] As for the crystal structure, a rhombohedron phase did not appear by the subdopant aluminum 2O3, but the cubic was stabilized to the room temperature. The result of 800 degrees C [which was measured like the example 1] ionic conductivity is shown in Table 3. $x+y < 0.16$ showed ionic conductivity higher than the value 2×10^{-2} of YSZ in 800 degrees C.

[0036] In addition, although ionic conductivity decreases slightly when little addition of SiO2 is carried out as sintering assistant **, the relative effect does not change.

Table [] 3 material Conductivity (ohm-1cm-1)

0.96ZrO2-0.02Sc2O3-0.02Aluminum 2O3 2.4×10^{-2} 0.94ZrO2-0.04Sc2O3-0.02aluminum 2O3 3.1×10^{-2} 0.92ZrO2-0.06Sc2O3-0.02aluminum 2O3 6.2×10^{-2} 0.90ZrO2-0.08Sc2O3-0.02aluminum 2O3 7.3×10^{-2} 0.88ZrO2-0.10Sc2O3-0.02aluminum 2O3 7.1×10^{-2} 0.86ZrO2-0.12Sc2O3-0.02aluminum 2O3 2.4×10^{-2} 0.84ZrO2-0.14Sc2O3-0.02aluminum 2O3 2.1×10^{-2}

[0037] (Example 4)

(1-x-y) After blending ZrO2-xSc2O3-yAl 2O3 ($0.07 \leq x+y \leq 0.13$ and $0.005 \leq y \leq 0.02$) by the chemical composition shown in Table 4, it mixed enough, baking was performed for what was cast to ** let with a 20mmphi thickness of 2mm at the temperature of 1620 degrees C for 60 hours in air, and ion ***** was produced. After identifying the generation phase of a sample by the powder X diffraction and carrying out the sweep of the ionic conductivity on the frequency of 10Hz - 1MHz by the impedance meter, it measured by performing an impedance plot.

[0038] As for the crystal structure, a rhombohedron phase did not appear by the subdopant aluminum 2O3, but the cubic was stabilized to the room temperature. The result of 800 degrees C [which was measured like the example 1] ionic conductivity is shown in Table 4. $0.07 \leq x+y \leq 0.13$ showed the high ionic conductivity of 3 times from the value 2×10^{-2} of YSZ in 800 degrees C.

[0039] In addition, although ionic conductivity decreases slightly when little addition of SiO2 is carried out as sintering assistant **, the relative effect does not change.

table 4 Material Conductivity (ohm-1cm-1) 0.93ZrO2-0.065Sc2O3-0.005aluminum 2O3 6.8×10^{-2} 0.92ZrO2-0.075Sc2O3-0.005aluminum 2O3 7.5×10^{-2} 0.91ZrO2-0.085Sc2O3-0.005aluminum 2O3 8.8×10^{-2} 0.90ZrO2-0.095Sc2O3-0.005aluminum 2O3 10.3×10^{-2} 0.89ZrO2-0.105Sc2O3-0.005aluminum 2O3 10.6×10^{-2} 0.88ZrO2-0.115Sc2O3-0.005aluminum 2O3 8.9×10^{-2} 0.87ZrO2-0.125Sc2O3-0.005aluminum 2O3 7.2×10^{-2} 0.86ZrO2-0.135Sc2O3-0.005aluminum 2O3 5.9×10^{-2}

[0040] (Example 5) Drawing 3 is drawing showing the example of composition of the solid fuel cell of the single cell which used the material of this invention. For 1, as for a solid electrolyte and 3, in the cell composition of this example, an oxygen electrode and 2 are [a fuel electrode and 4] interchange connectors. nickel-ZrO2 was used for the fuel electrode, and LaCrO3 was used for the interchange connector for LaMnO3 which doped Sr as an oxygen electrode. The creation method of a single cell is as follows. LaMnO3 which doped Sr first is roasted to the sintered compact of ceramics by the usual solid-phase-reaction method, and the ceramic thin film of a solid electrolyte is roasted at 1600 degrees C of formation by the doctor blade method on it. In addition, a fuel electrode and an interchange connector are calcinated and made from 1300 degrees C and 1200 degrees C by the single film sequential laminating forming method, respectively.

[0041] Next, the example of measurement shows the effect of this example. In drawing 3, thickness of an oxygen electrode 1 and the fuel electrode 3 was set to 1mm; thickness of a solid electrolyte 2 was set to 0.1mm, thickness of an interchange connector was set to 1mm, and the single cell of 20mmphi was formed. The current (current density)-voltage characteristic of the single cell in 800 degrees C of H2-air atmosphere in case the material of a solid electrolyte 2 is 0.88ZrO(s)2-

0.115Sc₂O₃-0.005aluminum 2O₃ is shown in drawing 4 . It is the property of the conventional example shown for comparison of the curve by the side of YSZ. Thus, the cell property with this example better than the conventional example, i.e., the current-voltage characteristic, was acquired. When the material of this invention was similarly used as a solid electrolyte, the whole of the cell property was better than the conventional example.

[0042]

[Effect of the Invention] It has conductivity 4 times the BE **** of this. oxygen ion ***** YSZ conventionally used by the device of the 2nd dopant although it was not able to use as a material, since 2OZrO₂-Sc₃ system was the instability of the crystal structure although it has the highest ionic conductivity by the zirconia system as explained above -- a ratio -- And the mechanical strength to a heat cycle succeeded in obtaining a small material of aging of hot conductivity strongly by stabilizing a cubic to a room temperature structurally. this invention makes a big contribution to low-temperature operation-ization of a solid fuel cell.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] (a) $0.88\text{ZrO}_2\text{-}0.115\text{Sc}_2\text{O}_3\text{-}0.005\text{aluminum } 2\text{O}_3$ (b) $0.88\text{ZrO}_2\text{-}0.12\text{Sc } 2\text{O}_3$ X-ray diffraction pattern.

[Drawing 2] (a) $0.88\text{ZrO}_2\text{-}0.115\text{Sc}_2\text{O}_3\text{-}0.005\text{aluminum } 2\text{O}_3$ (b) $0.88\text{ZrO}_2\text{-}0.12\text{Sc } 2\text{O}_3$ Ionic conductivity.

[Drawing 3] The block diagram of the solid fuel cell of the single cell of an example 5.

[Drawing 4] The current-voltage characteristic view of the single cell of an example 5.

[Translation done.]